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Factors Controlling In Situ Uranium and Technetium Bio-Reduction and Reoxidation at the NABIR Field Research Center

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RESULTS TO DATE: PROGRESS REPORT May 5, 2004 Factors Controlling In Situ Uranium and Technetium Bio-Reduction and Reoxidation at the NABIR Field Research Center

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Summary of Recent Field Testing: Extensive in situ (in ground) field testing using the push-pull method has demonstrated that indigenous microorganisms in the shallow (< 8 m) aquifer in FRC Areas 1 and 2 are capable of coupling the oxidation/fermentation of injected ethanol, glucose, or acetate to the reduction of U(VI) and Tc(VII). Despite highly variable initial (prior to testing) contaminant concentrations (pH: 3.3-7.2; Nitrate: 0.1-140 mM; U(VI): 1-12 uM; Tc(VII): 200-15000 pM), sequential donor additions resulted in increased rates of microbial activity (Denitrification: 01.-4.0 mM/hr; sulfate reduction: 0- 0.03 mM/hr; U(VI) reduction: 10-4 to 10-3 uM/hr; Tc(VII) reduction: 4-150 pM/hr) in all wells tested. Tc(VII) reduction and denitrification proceeded concomitantly in all tests. U(VI) reduction was concomitant with Fe(II) production in Area 1 but little Fe(II) was detected under sulfate reducing conditions in Area 2. Reoxidation of U(IV) (precipitated in the vicinity of the wells during previous tests) but not Tc(IV) was observed when injected test solutions contained initial nitrate concentrations > ~ 20 mM. Field data and laboratory studies suggest that U(IV) is likely oxidized by Fe(III) minerals produced by enzymatic Fe(II) oxidation or by Fe(II) oxidation by nitrite. U(IV) reoxidation rates (10-3 to 10-2 uM/hr) were somewhat larger than U(VI) reduction rates indicating that sustained nitrate removal will be necessary to maintain the stability of U(IV) in this environment. The production of metal sulfides following addition of sulfate was shown to reduce U(IV) reoxidation rates in field tests conducted in Area 2. Added FRC humics increased the rate of U(VI) reduction in some field tests but not in laboratory microcosms, although added humics increased the survival of FRC isolates in low pH groundwater. Several denitrifying organisms have been isolated from Area 1 that tolerate relatively low pH (4.5-5.5). Increased pH resulting from microbial activity during biostimulation in portions of the site with low (< 4) initial pH results in the formation of ~ 1-2 g/L of metal hydroxide precipitates that gradually reduce hydraulic conductivity and create locally high concentrations of potentially toxic metals (Al, Ni). Interpretations of field tests are supported by the results of laboratory studies with groundwater and sediments at the University of Oklahoma and by the results of geochemical and reaction path modeling performed on selected field tests at PNNL. Additional support for these conclusions are provided by the results of microbial sampling by Aaron Peacock and David White at the University of Tennessee; Joel Kostka at the University of Florida, and by Chris Schadt at ORNL, which confirm that donor additions resulted in the creation of anaerobic conditions and the growth of metal reducing organisms.

Ongoing Field Activities: An extensive series of field tests has been initiated to confirm the results of preliminary tests in Areas 1 and 2, which indicated that added humics increased rates of U(VI) reduction. Detailed information on vertical variations on porewater geochemistry are being obtained through the use of Multilevel Samplers (MLS) installed in sets of three wells in Areas 1 and 2. Tracer tests conducted in the MLS wells will provide a quasi-three-dimensional description of the portion of the aquifer interrogated during push-pull tests. The MLS will also be used to investigate geochemical and microbial community changes resulting from donor additions in prepared sediments deployed in the MLS cells and to directly monitor U(IV) reoxidation following biostimulation. Loss of hydraulic conductivity has been observed in field tests conducted with low pH, high nitrate groundwater but not with moderate pH, low nitrate groundwater. This is likely due to a combination of three factors: precipitation of dissolved solids, growth of biomass, generation of N2 gas, and well-screen clogging. Acid treatment of wells has partially restored

hydraulic conductivity but values are still smaller than pre-test levels. Field tests will be conducted in collaboration with Susan Hubbard (LBNL) in Areas 1 and 2 to see if precipitate, biomass, or gas production can be detected and quantified using noninvasive geophysical methods. The effect of biomass and gas production on hydraulic conductivity of site sediments is also being investigated in a series of laboratory experiments conducted in collaboration with Mart Oostrom at EMSL. Reoxidation of biogenic U(IV) by nitrate is a critical factor affecting the long-term stability of U(IV) in this environment. We have recently initiated a series of field tests to examine the role of biogenic sulfide on the stability of U(IV). Initial laboratory tests suggest that enhanced sulfide production (e.g. by adding sulphate) can reduce the rate of U(IV) reoxidation by nitrate, O2, and other oxidants. Collectively our project results suggests that bioimmobilization of Tc(VII) and U(VI) should be possible at the FRC using a permeable reactive barrier consisting of three defined zones (1) pH adjustment (2) denitrification and Tc(VII) reduction, and (3) U(VI) reduction. This hypothesis is being tested in intermediate (~2 m)-scale physical models deployed at Areas 1 and 2. The physical models have been in operation for approximately 8 months, and preliminary results indicate that essentially complete U(VI) and Tc(VII) removal can be achieved with pore water velocities of ~ 8 cm/day, which are comparable to site groundwater velocities. Recent sediment sampling was conducted to verify the oxidation state of U and Tc in these sediments. These samples will be analyzed by several collaborators including Ken Kemner and Shelly Kelly at Argonne National Laboratory; Joe Stucki at the University of Illinois; and Jim McKinley and John Zachara at PNNL. Additional sampling is planned to identify changes in microbial community structure that occur along the flow paths in these models. This detailed information should provide us a nearly complete description of the biogeochemical processes that will occur as this complex, contaminated groundwater interacts with a biologically active treatment zone in the subsurface.

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COLLABORATIONS: University of Oklahoma PNNL ORNL